APPENDIX I

PROCESS TECHNICAL BACKGROUND

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APPENDIX I

PROCESS TECHNICAL BASELINE

I1.0 INTRODUCTION

The purpose of this appendix is to capture, in one place, any background information that contributes to understanding material balance calculations and physical properties that is not otherwise captured in Appendix A.

Section I2.0 establishes a master set of components to be carried by the Hanford Tank Waste Operation Simulator (HTWOS).

Section I3.0 provides background on some of the important phase equilibrium phenomenon that occurs in the Hanford Site waste solutions.

Section I4.0 explains how physical properties can be calculated, specifically liquid density and viscosity.

Section I5.0 contains background information pertaining to phenomenon in solid-liquid systems.

Section I6.0 summarizes the most recent knowledge with respect to waste solubilities of wastes and how sufficient caustic leaching is at removing constituents from solids.

Section I7.0 is reserved for documenting how private contractor flowsheets impact the overall Hanford Site material balance.

Section I8.0 documents the methodology used for determining the waste oxide loading in glass.

This document justifies process performance assumptions and various methods used for flowsheet calculations.

This appendix is intended to be a living document that will be updated to reflect changes in how HTWOS does its calculations.

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I2.0 MASTER SET OF COMPONENTS FOR MASS BALANCES

The purpose of this section is to identify a master set of radionuclide and chemical components which encompasses the stream definition needs of staging plans, sequence studies, process baseline, and performance assessments. Missing values for the components of this master set flags a characterization need.

Historically, the mass balances for tank waste management studies have reflected different levels of stream definition consistent with the study's requirements. For example, the Phase 1 low-activity waste (LAW) feed envelopes are defined in terms of 20 chemical components, 6 non-transuranic isotopes, and several transuranic (TRU) isotopes. Phase 1 high-level waste (HLW) feed compliance, on the other hand, is defined in terms of 35 chemical components and 21 isotopes. For U.S. Nuclear Regulatory Commission (NRC) classification purposes, tracking alpha emitting transuranium nuclides (>5 year half-life) and eight other long-lived and short-lived radionuclides is necessary.

The interim performance assessment considers 10 isotopes for the inadvertent intruder scenario, 12 isotopes for the groundwater scenario with geochemical retardation, and 14 isotopes for the groundwater scenario without geochemical retardation. In all, the performance assessment tracks 28 radionuclides.

Generally, waste metals are tracked in material balances as elements, appearing as their oxide equivalent for the first time in the glass effluent from the melter. Anionic species (Cl, CO_3, F, NO_2, NO_3, OH, sulfate, and total organic carbon [TOC]) account for most of the volatility from melters, phosphate being an exception.

For metals that have a bearing on chemical consumption during caustic leaching, however, certain conventions have been adopted for representing those components in the liquid phase. The fraction of the aluminum solubilized during leaching is tracked as the $Al(OH)_4^-$ anion. No attempt is made to differentiate between this tetrahydroxyaluminum anion and its dehydrated cousin AlO_2^- which may actually be present in highly concentrated solutions.

The current Hanford Tank Waste Operation Simulator (HTWOS) convention is to disregard Cr valence initially and carry all Cr as *Cr(Total)*. Chromium solubilized during caustic leaching will still be tracked as $Cr(OH)_4^-$, recognizing that it probably converts to Cr(VI). This convention allows us to differentiate Cr that is leached from Cr that was initially in solution. It is fortuitous that caustic leaching ($Cr(OH)_3$ to $Cr(OH)_4^-$) and permanganate leaching (to CrO_4^{-2}) each consume a mole of hydroxide per mole of $Cr(OH)_3$ so it isn't necessary to know the final valence to account for hydroxide consumption during leaching. In previous flowsheets, all soluble chromium was tracked as $Cr(OH)_4^-$ even though the thermodynamically preferred species in alkaline solution is CrO_4^{-2}. There is convincing empirical evidence that soluble Cr(III) does not persist in solution, either converting to Cr(VI), or precipitating as a Cr(III) compound.

Table I2-1 lists the components required for various purposes, the most likely sources of information on those constituents, and the components that will be tracked in the *TFC Operation and Utilization Plan* (TFC O&UP) master set of components. "?" means there is currently some question about where the value will come from, M* radionuclide carried as mass for mass balance calculations, then converted to radionuclide outside of HTWOS

Table I2-1. TFC Operation and Utilization Plan Master Set of Mass Balance Constituents. (6 Sheets)

Requirements					TFC O&UP Components
Envelope A,B,C Table TS-7.1 Table TS-7.2 (BNFL 2000a)	Envelope D Table TS-8.1 Table TS-8.2 Table TS-8.3 Table TS-8.4 (BNFL 2000b)	Class C 10CFR61.55 Table 1 Table 2	Performance Assessment	HazMat (Boothe 1996) or NRC	
	Ag			Ag	Ag
Al	Al				Al
					A1(OH)4
	As				As
	B				B
Ba	Ba				Ba
	Be				Be
	Bi				Bi
Ca	Ca				Ca
Cd	Cd			Cd	Cd
	Ce				Ce
	Co				Co
Cr	Cr			Cr	Cr
					Cr(OH)4
	Cs				Cs
	Cu			Cu	Cu
Fe	Fe			Fe	Fe
					H
Hg	Hg			Hg	Hg

Table I2-1. TFC Operation and Utilization Plan Master Set of Mass Balance Constituents. (6 Sheets)

Requirements					TFC O&UP Components
Envelope A,B,C Table TS-7.1 Table TS-7.2 (BNFL 2000a)	Envelope D Table TS-8.1 Table TS-8.2 Table TS-8.3 Table TS-8.4 (BNFL 2000b)	Class C 10CFR61.55 Table 1 Table 2	Performance Assessment	HazMat (Boothe 1996) or NRC	
K	K				K
La	La				La
	Li				Li
	Mg				Mg
	Mn				Mn
	Mo				Mo
	Na			Na	Na
	Nd				Nd
Ni	Ni			Ni	Ni
Pb	Pb			Pb	Pb
	Pd				Pd
					Pr
	Pu				Pu
	Rb				Rb
	Rh				Rh
	Ru				Ru
	Sb			Sb	Sb
	Se			Se	Se
	Si				Si
Sr	Sr				Sr
	Ta				Ta
Tc	Tc				Tc
	Te				Te
	Th				Th

Table I2-1. TFC Operation and Utilization Plan Master Set of Mass Balance Constituents. (6 Sheets)

Requirements					TFC O&UP Components
Envelope A,B,C Table TS-7.1 Table TS-7.2 (BNFL 2000a)	Envelope D Table TS-8.1 Table TS-8.2 Table TS-8.3 Table TS-8.4 (BNFL 2000b)	Class C 10CFR61.55 Table 1 Table 2	Performance Assessment	HazMat (Boothe 1996) or NRC	
	Ti				Ti
	Tl			Tl	Tl
U	U			U	U
	V				V
	W				W
	Y				Y
	Zn				Zn
	Zr				Zr
Cl	Cl			Cl	Cl
	CN				CN
CO3	CO3				CO3
F	F			F	F
	NH3				NH3
NO2	NO2			NO2	NO2
NO3	NO3			NO3	NO3
				OH	OH
PO4	PO4				PO4
SO4	SO4			SO4	SO4
					H2O
					Separable Organic
TOC	TOC			Organic Carbon	Organic Carbon
			Ac-227		Ac-227

Table I2-1. TFC Operation and Utilization Plan Master Set of Mass Balance Constituents. (6 Sheets)

Requirements					TFC O&UP Components
Envelope A,B,C Table TS-7.1 Table TS-7.2 (BNFL 2000a)	Envelope D Table TS-8.1 Table TS-8.2 Table TS-8.3 Table TS-8.4 (BNFL 2000b)	Class C 10CFR61.55 Table 1 Table 2	Performance Assessment	HazMat (Boothe 1996) or NRC	
Am-241	Am-241	Am-241	Am-241		Am-241
Am-243		Am-243	Am-243		Am-243
	C-14	C-14	C-14	C-14	C-14
Co-60	C-60				Co-60
		Cm-242		Cm-242	Cm-242
Cm-243	Cm-243	Cm-243			Cm-243
Cm-244	Cm-244	Cm-244			Cm-244
			Cm-245		?
Cs-137	Cs-137	Cs-137	Cs-137	Cs-137	Cs-137
					Ba-137
	Eu-152				Eu-152
Eu-154	Eu-154				Eu-154
Eu-155	Eu-155				Eu-155
	H-3		H-3		H-3
	I-129	I-129	I-129	I-129	I-129
			Nb-93m		Nb-93m
		Ni-63		Ni-63	Ni-63
Np-237	Np-237	Np-237	Np-237	Np-237	Np-237
			Pa-231		Pa-231
Pu-328	Pu-238	Pu-238		Pu-238	Pu-238
Pu-239	Pu-239	Pu-239	Pu-239	Pu-239	Pu-239
Pu-240		Pu-240	Pu-240	Pu-240	Pu-240
Pu-241	Pu-241	Pu-241		Pu-241	Pu-241
Pu-242		Pu-242		Pu-242	Pu-242

Table I2-1. TFC Operation and Utilization Plan Master Set of Mass Balance Constituents. (6 Sheets)

Requirements					TFC O&UP Components
Envelope A,B,C Table TS-7.1 Table TS-7.2 (BNFL 2000a)	Envelope D Table TS-8.1 Table TS-8.2 Table TS-8.3 Table TS-8.4 (BNFL 2000b)	Class C 10CFR61.55 Table 1 Table 2	Performance Assessment	HazMat (Boothe 1996) or NRC	
		Pu-244			?
			Ra-226		Ra-226
			Ra-228		Ra-228
	Sb-125				Sb-125
			Se-79		Se-79
			Sm-151		Sm-151
	Sn-126		Sn-126		Sn-126
Sr-90	Sr-90	Sr-90	Sr-90	Sr-90	Sr-90
					Y-90
Tc-99	Tc-99	Tc-99	Tc-99	Tc-99	Tc-99
			Th-229		Th-229
			Th-232		Th-232
					U-232
	U-233		U-233		U-233
			U-234		U-234
	U-235		U-235		U-235
			U-236		U-236
			U-238		U-238
			Zr-93		Zr-93
				Butanol	?
				DBP/TBP	?
				EDTA	?

Note: See Appendix B for the current discussion of the origin of component values.

There is considerable overlap between the available sources of composition data, but no single source satisfies the requirements of all the studies (staging plans, sequence study, and process baseline). The global standard inventory tracks 26 chemical species; the standard tank-by-tank inventory tracks a slightly different set. The global standard inventory will have to be supplemented with additional sources of data if non-standard constituents are to be tracked.

I2.1 REFERENCES

BNFL, 2000a, *Interface Control Document for Low-Activity Waste Feed*, BNFL-5193-ID-19, Rev. 4d, BNFL, Inc., Richland, Washington.

BNFL, 2000b, *Interface Control Document for High-Level Waste Feed*, BNFL-5193-ID-20, Rev. 4a, BNFL, Inc., Richland, Washington.

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I3.0 EVALUATION OF SUPERNATE CHEMISTRY

I3.1 ALUMINUM SOLUBILITY

The solubility of aluminum in the Na_2O-Al_2O_3-H_2O system is well documented in the literature. The soluble aluminum species present in Hanford tank waste is generally conceded to be $Al(OH)_4^-$, which has, in fact been confirmed by raman spectroscopy. Tetrahydroxyaluminate anion exists in equilibrium with gibbsite or sodium aluminate, depending on the hydroxide concentration and the overall ionic strength of the solution. The equilibrium equations that define aluminum solubility are:

$$Al(OH)_3 + OH^- = Al(OH)_4^-$$

$$Al(OH)_4^- + Na^+ + nH_2O = NaAlO_2 \cdot (2+n)H_2O$$
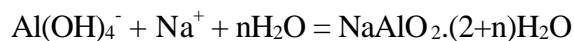
Since precipitated sodium aluminate solids contain waters of hydration, variations in the activity of water can significantly alter the solubility. The activity of water is, in turn, highly dependent on the total ionic strength of species not explicitly shown in the equilibrium equations (Reynolds 1995). From the above equations, the activity of OH^- and Na^+ is also important in defining the solubility of aluminum. Since ions in solution are solvated with water, the activity of water also affects the activity of the solvated species.

The presence of other salts in the Na_2O-Al_2O_3-H_2O system affects the solution field of aluminum. An early study (Barney 1976) showed that aluminum solubility as a function of hydroxide concentration dramatically shifts in the presence of other saturated salts (nitrate, nitrite, carbonate, and sulfate). Others have observed this complex phenomenon as well (Herting and Cleavenger 1983; Reynolds and Herting 1984; Herting et al. 1986).

Barney's results indicate a depressed aluminum solubility in the range above 2 M OH^- where soluble aluminum is in equilibrium with sodium aluminate. The depression of sodium aluminate solubility in waste simulants has been studied extensively in the Hanford labs (Herting and Cleavenger 1983; Reynolds 1995). Regression of the solubility data provides an equation for calculating the sodium aluminate solubility (Reynolds and Herting 1984).

$[NaAlO_2] = 5.304 - 0.0550(temp) - 0.502[OH^-] + 0.000413(temp)^2 + 0.00282(temp)[OH^-] - 0.00189(temp)[NO_3^-] - 0.00150(temp)[NO_2^-]$

Valid Ranges:
temp from 60 ºC to 100 ºC
[OH^-] from 2.0 to 6.6 M
[NO_2^-] from 2.0 to 6.2 M
[NO_3^-] from 1.7 to 5.0 M

The authors suggest that this equation will predict solubility within about 10 percent. The solubility of sodium aluminate projected from the Reynolds-Herting equation is considerably lower than the solubilities reported by Barney.

Increasing the water content of aluminum-bearing liquids may result in the precipitation of gibbsite. Absorption of CO_2 from the air, which depletes free hydroxide, may have a similar effect. For liquids that have crossed over the gibbsite phase boundary, an addition of Na_2O (as caustic) is usually sufficient to resolubilize gibbsite.

I3.2 PHOSPHATE FLUORIDE SOLUBILITY

Another phase diagram pertinent to managing Hanford wastes is the Na_3PO_4-NaF-H_2O system (Mason and Ashcroft 1939). While sodium phosphate is reasonably soluble by itself, the presence of small amounts of sodium fluoride depresses solubility dramatically due to the formation of the double salt $Na_7F(PO_4)_2$ $19H_2O$. The phase behavior of this system is further complicated in the presence of hydroxide since a protonated phosphate and a deprotonated phosphate behave differently. The hydroxide concentration is also affected by the equilibrium of the Na_2O-Al_2O_3-H_2O system.

The implications of the Na_3PO_4-NaF-H_2O system is that tanks with high phosphate and fluoride could contain appreciable amounts of this low solubility double salt that won't dissolve with moderate dilution anticipated for retrieval.

I3.3 REFERENCES

Barney, G. S., 1976, *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*, ARH-ST-133, Atlantic Richfield Hanford Company, Richland, Washington.

Herting, D. L. and R. M. Cleavenger, 1983, *Solubility Phase Diagram - Final Report*, SD-WM-TI-078, Rockwell Hanford Operations, Richland, Washington.

Herting, D. L., T. Welsh, and D. A. Reynolds, 1986, *Gibbsite Equilibrium in Simulated Liquid Waste*, SD-WM-TI-211, Rockwell Hanford Operations, Richland, Washington.

Mason and Ashcroft, 1939, Trisodium Phosphate-Sodium Fluoride Studies and Analytical Methods, Industrial and Engineering Chemistry, Vol. 31, No. 6, June, 1939.

Reynolds, D. A., 1995, *Practical Modeling of Aluminum Species in High-pH Waste*, WHC-EP-0872, Westinghouse Hanford Company, Richland, Washington.

Reynolds, D. A. and D. L. Herting, 1984, *Solubilities of Sodium Nitrate, Sodium Nitrite, and Sodium Aluminate in Simulated Nuclear Waste*, RHO-RE-ST-14P, Rockwell Hanford Operations, Richland, Washington.

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I4.0 PHYSICAL PROPERTIES

I4.1 SOLUTION DENSITY

The purpose of Section I4.1 is to explain the liquid density model used by HTWOS, and to document information about alternate methods of calculating density.

The availability of various models for calculating solution density has sometimes caused tank waste management studies to be inconsistent with each other. A model regressed by Reynolds and Herting (1984b) from data on 50 moderately to highly concentrated simulants, in use since 1984, accounts for AlO_2, NO_2, NO_3 and OH, and includes a temperature term. There is also a density model regressed by Agnew and Watkin (1994) from extensive laboratory measurements on actual waste samples. The Agnew and Watkin model accounts for Al, Na, NO_2, NO_3 and OH.

Recently, the Environmental Simulation Program (ESP) of OLI Systems, Inc. has seen increased usage at Hanford. The ESP calculates solution density from basic principles while modeling the complicated chemistry of electrolyte solutions.

The density model used in conjunction with HTWOS was borrowed from the TWRS Process Flowsheet or *TWRS Privatization Process Technical Baseline* (Orme et al. 1996). The coefficients for the model were developed from earlier plutonium-uranium extraction (PUREX) flowsheet studies. The HTWOS density model assumes direct, first-order proportionality between component concentration and density.

All of the models do a reasonable job of predicting density, but the HTWOS density model is the least cumbersome to use in conjunction with HTWOS. To illustrate the consistency of two of these models, Perry's Handbook density values for $NaNO_3$ solutions at 20 and 40 $^{\circ}$C were interpolated to 25 $^{\circ}$C. Table I4-1 and Figure I4-1 compare the Handbook density to an ESP simulation and the HTWOS density model. $NaNO_3$ was selected for this comparison because it is the primary soluble component in all tank waste. Over a wide range of concentration, the difference is less than 1 percent.

I4.1.1 HTWOS Density Model

Density calculations in earlier TWRS Process Flowsheet and Privatization Process Technical Baseline are based on the assumption that individual component contributions are proportional to component molarity, and individual component contributions are additive. The flexibility to add or delete components from the density determination is an attractive feature of this model:

$$d_T = d_w + 3(\gamma_i M_i) \hspace{3cm} \text{Equation 1}$$

Table I4-1. $NaNO_3$ Solution Density.

ESP's density @ 20 °C	Perry's Handbook		Wt%	Perry's molarity@ 25 °C	Perry's density @ 25 °C	ESP's density @ 25 °C	HTWOS density @ room temperature
	Density @ 20 °C	Density @ 40 °C					

1.0049	1.0049	0.9986	1	0.118	1.0033	1.0035	1.0060
	1.0117	1.0050	2	0.238	1.0100	1.0102	1.0121
	1.0254	1.0180	4	0.482	1.0236	1.0237	1.0246
	1.0532	1.0447	8	0.989	1.0511	1.0513	1.0505
	1.0819	1.0724	12	1.524	1.0795	1.0800	1.0777
	1.1118	1.1013	16	2.088	1.1092	1.1099	1.1065
1.1448	1.1429	1.1314	20	2.682	1.1400	1.1413	1.1368
	1.1752	1.1629	24	3.310	1.1721	1.1742	1.1688
	1.2085	1.1955	28	3.970	1.2053	1.2087	1.2025
	1.2256	1.2122	30	4.314	1.2223	1.2266	1.2200
	1.2701	1.2560	35	5.215	1.2666	1.2733	1.2660
1.3311	1.3175	1.3027	40	6.183	1.3138	1.3230	1.3153

Figure I4-1. NaNO$_3$ Solution Density.
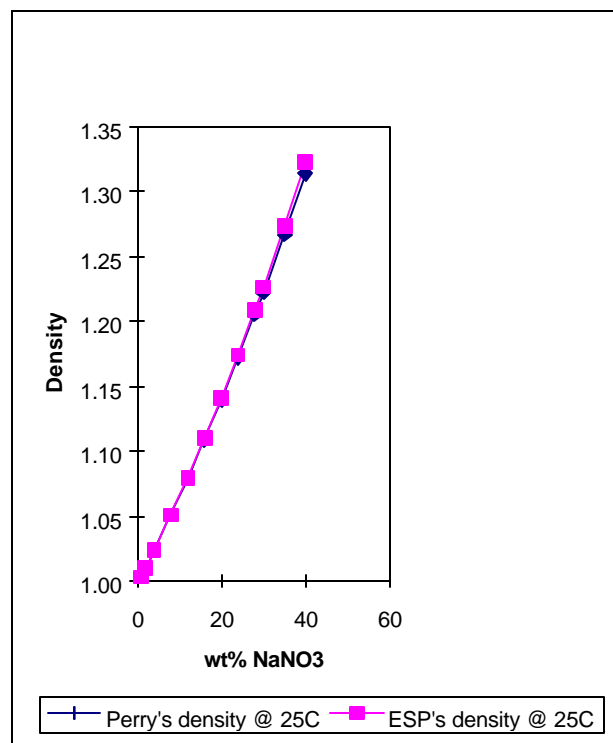
Substitution and algebraic manipulation yields an equivalent formula in terms of individual component mass (m_i) and total mass (m_T) of the solution:

$$d_T = m_T d_w/(m_T - 1000 \cdot 3(\gamma_i m_i/mw_i)) \qquad \text{Equation 2}$$

d_T is solution density
d_w is water density
m_T is total mass
γ_i are the density coefficients
m_i are the component masses
mw_i are the component molecular weights.

In the HTWOS material balance, solute mass information is available rather than molarity so Equation 2 is preferred. Table I4-2 provides the coefficients that have been used historically.

Table I4-2. Constants and Coefficients for the HTWOS Density Model.

Component	mw_i	γ_i (historical)	γ_i (ESP based)
$Al(OH)_4^-$	95.01	0.1553	0.04
Carbonate	60.01	0.0989	
Fluoride	18.998	0.028	
Nitrite	46.0	0.051	
Nitrate	62.0	0.051	0.054
Hydroxide	17.01	0.028	
Sulfate	96.058	0.061	
Uranyl ion	270.027	0.318	

The origin of the historical aluminate coefficient was traced to aluminum nitrate. An ESP model of aluminum nitrate solution verified that the historical density coefficient is consistent with a much heavier aluminum nitrate molecule ($mw_i = 213$) rather than sodium aluminate ($mw_I = 82$). The historical coefficient appears to overstate aluminum's contribution. Adjustment of the aluminum coefficient was justified, so we developed an alternate, ESP-based coefficient that is currently in use by HTWOS. The other historical coefficients appear reasonable.

The total mass divided by solution density yields total volume (V_T). An equation to calculate total volume directly from mass data is easily derived from the above equation:

$$V_T = [m_T - 1000 \cdot 3(\gamma_i m_i/mw_i)]/d_w \qquad \text{Equation 3}$$

I4.1.2 Densities Calculated by Environmental Simulation Program

The ESP is currently in use at the Hanford site to perform thermodynamic equilibrium calculations on electrolyte solutions. The ESP calculates the density of aqueous solutions by a partial molal volume approach. The details of this methodology can be found in standard handbooks (Zemaitis et al. 1986). The following discussion documents that we have found ESP-calculated densities to be in excellent agreement with literature values for both simple and complex salt solutions.

I4.1.2.1 Single-Component Solutions. The following tables compare Chemical Engineers' Handbook (Perry and Chilton 1973) density data to ESP-calculated density for single-component electrolyte solutions. The handbook values are considered reliable. Tables I4-3, I4-4, I4-5, and I4-6 are for sodium nitrate, sodium hydroxide, sodium carbonate, and sodium sulfate, respectively. These are common components in Hanford tank waste. How well ESP calculates density depends, of course, on the quality of the data in its database. For these four compounds, there is excellent agreement between ESP-calculated density and the Chemical Engineers' Handbook.

Table I4-3. Sodium Nitrate Density.

Wt %	40 ^{o}C		80 ^{o}C	
	Handbook	ESP	Handbook	ESP
1	0.999	0.998	0.978	0.978
12	1.072	1.072	1.048	1.048
24	1.163	1.162	1.135	1.132
35	1.256	1.255	1.226	1.217

ESP = Environmental Simulation Program
ESP density is within 1 percent of handbook.

Table I4-4. Sodium Hydroxide Density.

Wt %	40 ^{o}C		80 ^{o}C	
	Handbook	ESP	Handbook	ESP
1	1.003	1.002	0.982	0.982
8	1.078	1.066	1.056	1.044
16	1.164	1.140	1.141	1.115
24	1.251	1.222	1.226	1.192

ESP = Environmental Simulation Program
ESP density is within 3 percent of handbook. Disparity increases with concentration and temperature.

Table I4-5. Sodium Carbonate Density.

Wt %	30 ^{o}C		80 ^{o}C	
	Handbook	ESP	Handbook	ESP
1	1.006	1.006	0.981	0.982
4	1.036	1.036	1.010	1.010
14	1.142	1.141	1.112	1.103

ESP = Environmental Simulation Program
ESP density is within 1 percent of handbook.

Table I4-6. Sodium Sulfate Density.

Wt %	40 $^{\circ}$C		80 $^{\circ}$C	
	Handbook	ESP	Handbook	ESP
1	1.001	1.000	0.980	0.980
8	1.064	1.054	1.043	1.030
16	1.141	1.118	1.118	1.089

ESP = Environmental Simulation Program
ESP density is within 3 percent of handbook.
Disparity increases with concentration and temperature.

I4.1.2.2 Multi-Component Solutions. Density data for single-component solutions, such as those noted above, are usually tabulated across a wide range of concentration. Density values for waste-like, multi-component solutions of low to intermediate ionic strength are difficult to find. Typically, multi-component density data is found in conjunction with multi-component solubility data, i.e., only for *saturated* solutions. Large collections of multi-component solubility data (Linke 1965) are available. It is difficult to vouch for the accuracy of individual citations. The ESP-calculated density for several multi-component systems was cross-checked against some values found in this literature.

Density for saturated solutions of sodium nitrate and sodium chloride were calculated with ESP. Table I4-7 compares the results with literature (Linke 1965).

Table I4-7. Density of Saturated $NaNO_3$ - NaCl Solutions At 50 $^{\circ}$C.

Wt% $NaNO_3$	Wt% NaCl	Density (Linke 1965)	Density (ESP)
15.3	20.5	1.259	1.244
35.6	11.9	1.370	1.350
48.8	3.57	1.418	1.404

ESP = Environmental Simulation Program
ESP density is within 1 percent of literature.

Table I4-8 provides density data for the same system over a wide range of temperature. Linke's values are from different researchers.

Table I4-8. Density of Saturated $NaNO_3$ - NaCl Solutions.

Wt% $NaNO_3$	Wt% NaCl	Temp ^{o}C	Density (Linke 1965)	Density (ESP)
43.7	3.16	25	1.386	1.396
42.6	5.10	30	1.394	1.392
44.8	5.38	40	1.410	1.395
48.8	3.57	50	1.418	1.404
54.2	3.72	75	1.460	1.414
55.0	6.16	91	1.518	1.417
59.4	3.97	100	1.501	1.429

ESP = Environmental Simulation Program
ESP density is within 1 percent of literature below 60 ^{o}C.
Disparity increases (3 to 7 percent) at higher temperature.

Density for saturated solutions of sodium nitrate, sodium chloride, and sodium sulfate, all components in Hanford waste, were calculated with ESP. Table I4-9 compares the results with literature.

Table I4-9. Density of Saturated $NaNO_3$ - NaCl - Na_2SO_4 Solutions at 25 ^{o}C.

Wt% $NaNO_3$	Wt% NaCl	Wt% Na_2SO_4	Density (Linke 1965)	Density (ESP)
7.08	9.98	14.9	1.281	1.284
23.9	4.32	10.8	1.333	1.348
41.0	3.43	2.80	1.396	1.411

ESP = Environmental Simulation Program
ESP density is within 1 percent of literature.

Densities higher than calculated values have been observed by Hanford researchers in simulated waste solutions. Density for solutions of sodium nitrate, sodium nitrite, sodium aluminate, and sodium hydroxide have been calculated with ESP. Table I4-10 compares the results with literature (Reynolds and Herting 1984b).

Table I4-10. Density of $NaNO_3$ – $NaNO_2$ - $NaAlO_2$ – NaOH Solutions[a] At 60 °C.

Molality $NaNO_3$	Molality $NaNO_2$	Molality $NaAlO_2$	Molality NaOH	Density (Reynolds and Herting 1984)	Density ESP (WESOL)	Density ESP (Public)
6.26	9.05	3.80	5.22	1.57	1.50[b]	1.46[b]
5.48	7.36	2.53	8.85	1.54	1.48[b]	1.45[b]
4.50	5.50	1.85	11.28	1.53	1.47[b]	1.45[b]
3.95	4.91	4.69	5.22	1.51	1.50	1.46
3.43	4.91	2.67	8.85	1.51	1.48	1.45[b]
3.25	3.75	2.09	11.28	1.51	1.47[c]	1.45[c]

ESP = Environmental Simulation Program
ESP density is within 5 percent of literature. Typical of disparity at higher concentration.
[a] All solutions were also: [b] NO_3/NO_2 precipitate   [c] NO_2 precipitate
 0.051m sodium EDTA
 0.083m sodium citrate
 0.070m sodium phosphate
 0.070m sodium carbonate
 0.016m sodium sulfate

Table I4-11 compares ESP densities to the measured room temperature density of stock solutions containing $NaAlO_2$, NaOH, Na_2CO_3 and Na_2SO_4 (Reynolds and Herting 1984). Table I4-10 shows the ESP density using Hanford's WESOL database and the PUBLIC database provided with ESP.

Table I4-11. Density of $NaAlO_2$ – NaOH Solutions[a] at 25 ^{o}C.

Molality $NaAlO_2$	Molality NaOH	Density (Reynolds and Herting 1984)	Density ESP (WESOL)	Density ESP (PUBLIC)
2.03	9.22	1.386	1.377	1.365
1.74	7.90	1.395	1.331	1.321
1.08	8.21	1.350	1.308	1.302

ESP = Environmental Simulation Program
ESP density is within 5 percent of literature.
[a] All solutions were also:
0.070m sodium carbonate
0.014m sodium sulfate

Data in the preceding tables have shown that the disparity between measured and ESP-calculated density is greatest at high concentration and temperature, but always within 5 percent. ESP (WESOL) agrees better with measured density than ESP (PUBLIC), especially when there is no second phase formation.

The onset of precipitation appears to be another area of discrepancy between ESP and experimental data. In Table I4-10, it is noteworthy that ESP (WESOL and PUBLIC) predicts precipitates in the most highly concentrated waste simulants, while Reynolds and Herting found none. This has been observed elsewhere.

Experimentally, concentrated salt solutions have a tendency to supersaturate and remain somewhat stable for extended periods. This can be seen in the measured densities from Reynolds and Herting (1984) and others. Since ESP calculates the minimum free energy condition (thermodynamic equilibrium, i.e., it does not allow supersaturation), excess solute is not allowed to be in solution. This is advantageous from a practical standpoint because if ESP does not predict precipitation, then the solution is probably a comfortable distance from saturation. Keeping salts in solution is usually desirable for waste processing purposes.

ESP's primary disadvantage is that it is too cumbersome for everyday use. It appears to predict densities in reasonable agreement with literature values. It can be improved by upgrading the underlying thermochemical data base.

I4.1.3 Reynolds-Herting Density Model

In conjunction with an experimental study of solubility in complex salt solutions, Reynolds and Herting (1984a) reported a simple three-variable model which relates supernate density to the concentration of sodium, aluminate[1] and free hydroxide:

Molarity: Density = 1 + 0.038[Na] + 0.07[Al(OH)$_4$] - 0.015[free OH]

In an improved version of the same study, they reported the solution density of 263 sodium salt solutions (Reynolds and Herting 1984b). Fifty solutions were selected for regression, resulting in an equation with four composition variables and a temperature variable. Handbook values for the density of water at various temperatures were also included in the regression without appreciably affect the accuracy of the equation in the concentration range that was tested.

Molality: Density = 1.137 + 0.0240[NO$_2$] - 0.00134[NO$_2$][NO$_3$] + 0.0183{[AlO$_2$] + [OH] + [NO$_2$] + [NO$_3$]} - 0.00189(T)

Molarity: Density = 1.017 + 0.0587[AlO$_2$] - 0.01943[OH] - 0.000883[NO$_2$][NO$_3$] + 0.0459{[AlO$_2$] + [OH] + [NO$_2$] + [NO$_3$]} - 0.000505(T)

The regression coefficient for the above density model was $R^2 = 0.98$.

The above equations were spot checked by Reynolds and Herting with compositions that were not included in the regression set. The calculated density was very close to measured density.

I4.1.4 Agnew-Watkin Density Model

To improve on the initial Reynolds-Herting model, Agnew and Watkin (1994) worked with a data set of 400 Hanford supernate samples and identified five analytes that appeared to dominate the density. While data from radioactive supernate samples are readily available, the challenge of obtaining very accurate concentration and density measurements while working under hot cell conditions is a factor to consider in relation to the reliability of these data.

This large data set was pared to 196 samples which reported analytical results for all five analytes of interest. The samples ranged from 1 to 1.75 in density; only a handful of samples were above 1.5 and the majority were below 1.4. An eleven-constant equation relating density to the concentration of the five analytes was derived from this sample set.

Molarity: Density = 1 + 0.2{-0.0955[Al]^2 + 0.383[Al] - 0.0054[Na]^2 + 0.1096[Na] - 0.073[NO$_2$]^2 + 0.373[NO^2] + 0.00046[NO$_3$]^2 + 0.201[NO$_3$] + 0.0197[OH]^2 + 0.0077[OH]}

---

[1]Aluminate is believed to exist in the form Al(OH)$_4$$^-$ in solution. The dehydrated form (AlO$_2$$^-$) is frequently us interchangeably as in some of the following equations.

Comparing calculated density to measured density yielded the following observations:

The difference between calculated density and measured density was more than 0.1 for 11 of 196 samples.

The difference was less than 0.05 for 148 of 196 samples.

The average difference between calculated and measured density was 0.034.

For general purpose use, this model proved to be unreliable. Because of the squared terms in the equation, the model calculates unrealistic density for chemical add streams that do not contain all five analytes, and for waste streams that depart appreciably from the compositions used for the regression. This is a limitation common to many regressed models.

I4.1.5 Recommended Density Equation

Handbook values of solution density show a reasonably linear dependence on molarity over a fairly wide range. Figure I4-1 shows linear dependence quite clearly. Linear dependence is inherent in the HTWOS density equation.

ESP's input requirements disqualify it as a general purpose density model within the HTWOS modeling environment. HTWOS does not currently track inventory as a charge-balanced listing of molecular components, as required by ESP. Converting HTWOS stream inventory data into ESP compatible format would be cumbersome and difficult to maintain with an inventory that is still changing.

ESP usually calculates density in close agreement with tabulated values in standard reference books, and measured values in the literature. A potential use of ESP is selective cross-checking of densities determined by alternate methods. Of the four density methods discussed above, only ESP recognizes the onset of temperature- or composition-induced precipitation in concentrated solutions. None of the three density equations is capable of indicating second phase formation.

The Reynolds-Herting equation (and likewise the Agnew-Watkin equation) is limited to the components included in the regression, where the HTWOS density equation has the flexibility of adding components as new coefficients are determined. Reynolds-Herting has a temperature adjustment term where the HTWOS density equation does not (except the density of water can be adjusted).

The Reynolds-Herting and HTWOS equations have virtually the same form, differing primarily in the numerical value of the constants. Because of the small coefficient before the $[NO_2][NO_3]$ term in the R&H model, one can ignore it and approximate the density contribution of NO_2 and NO_3 as 0.0459 per molarity unit. The density contribution of AlO_2 and OH in the R&H molarity equation is 0.1046 and 0.0265 per molarity unit, respectively. A comparison of coefficients from the Reynolds-Herting and TWRS Flowsheet density correlations is interesting. These are compared in Table I4-12. This is further confirmation that the historical coefficients are reasonable.

Table I4-12. Comparison of Coefficients.

Component	Reynolds-Herting Coefficients	HTWOS coefficients
Al(OH)₄	0.105	0.04
Oxalate		
Carbonate		0.0989
Fluoride		0.028
Nitrite	0.046	0.051
Nitrate	0.046	0.051
Hydroxide	0.026	0.028
Phosphate		
Sulfate		0.061
Uranyl ion		0.318

The largest difference is in the coefficient for soluble aluminum. Previously in this discussion, a lower value was established based on ESP predictions.

I4.2 SOLUTION VISCOSITY

The viscosity of water is well known and changes dramatically with temperature. Figure I4-2 shows the temperature dependence. In the temperature range that would be encountered during normal tank farm operations, the viscosity of water can change by a factor of two or more. Over the same temperature range, the density of water changes relatively little (0.998 kg/m^3 at 20 $^{\circ}$C to 0.958 kg/m^3 at 100 $^{\circ}$C). Because the Reynolds number is inversely proportional to kinematic viscosity (viscosity/density), turbulent flow is achieved at lower velocities with hot water than with cold water.

Solutes vary in their effect on solution viscosity. On a wt% basis, NaOH and NaCO$_3$ have a similar effect, while the effect of NaNO$_3$ is relatively minor. This is illustrated in Figure I4-3 for three salt solutions at 20 $^{\circ}$C.
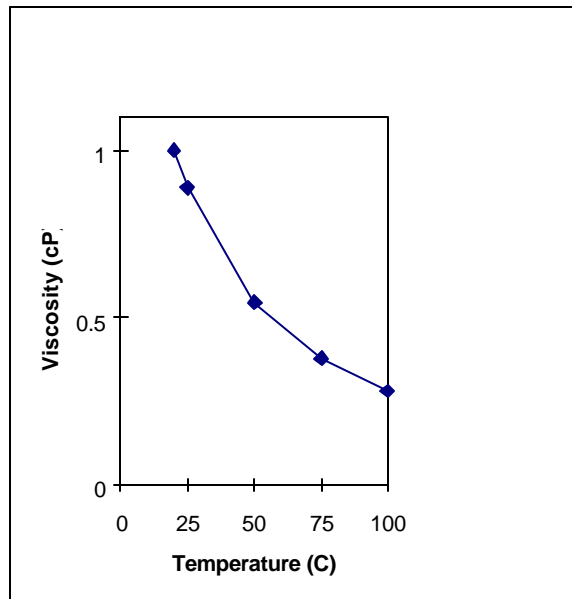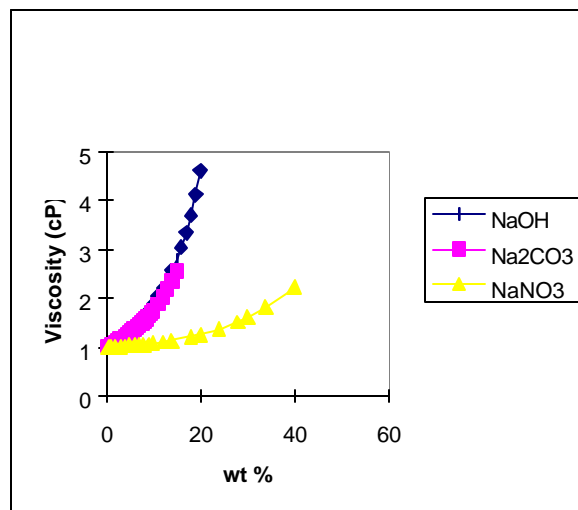
Figure I4-2. Viscosity of Water.

Figure I4-3. Viscosity at 20 °C.

While there is a well developed theoretical basis for estimating the viscosity of gases, there is no comparable theoretical basis for estimating liquid viscosities (Reid et al. 1987). Many viscosity-correlating methods have been proposed for organics and even aqueous-organic. Until recently, the correlations available for electrolytes did not adequately cover a wide range of temperature and solute concentration. To fill this void, one paper proposes a "hole model" to predict the viscosity of aqueous electrolytes containing mixed salts from very dilute solutions up to the molten salt regime (Zaltash and Ally 1992). The model has four parameters that can be evaluated from very little experimental data.

Viscosity data and correlations for single component solutions are readily available, but multicomponent correlations are difficult to find. Hanford workers have developed several correlations for evaporator slurries over the years which relate viscosity to density, but no correlation relating the viscosity to the concentration of individual components is available.

I4.2.1 Zaltash Viscosity Model

Zaltash and Ally proposed this model because no single correlation in the literature was capable of predicting viscosities over a wide range of temperature and over the complete concentration range, from very dilute to highly concentrated. Dispensing with the lengthy development of the "hole model," the correlation simplifies to the form:

$$u = u_0 \, e^{(E/RT)}$$

where u_0 is a characteristic of the salt mixture having negligible dependence on temperature and concentration (wt%) in solution. The exponential term captures concentration dependence and temperature dependence. E/R, the activation energy for viscous flow, is a second order polynomial:

$$E/R = A + B(wt\%) + C(wt\%)^2$$

where wt% is the concentration of the salt or salt mixture. The temperature is degrees Kelvin. Therefore, there are four parameters (u_0, A, B, C) to be determined for any salt or mixture of salts.

The data required to evaluate the parameters is minimal. The pre-exponential term (u_0) is evaluated from two viscosity measurements at one concentration (i.e., at two temperatures). It is a good idea to evaluate u_0 at more than one concentration and average the values.

Once u_0 is evaluated, simultaneous equations can be solved to evaluate A, B and C.

$$E/R = T(\ln u_T - \ln u_0) = A + B(wt\%) + C\,(wt\%)^2$$

The polynomial coefficients are evaluated from the viscosity of water (at two temperatures) and the viscosity of the salt solution at two different strengths (each at two temperatures).

The EXCEL SOLVER feature provides a quick way to solve for the Zaltash parameters by minimizing the square of the difference between experimental and calculated viscosity. This spreadsheet approach is very flexible and convenient, since all available data can be included in the evaluation. A sample output of this spreadsheet for NaOH solution is provided in Table I4-4, and for 241-AN-105 liquids in Table I4-5. This output records the conditions (wt% and temperature) of experimentally determined viscosity, the Zaltash parameters, and the calculated viscosity. There is also a block for predicting viscosities requiring the user to enter a wt% and temperature.

Note that the Zaltash model does not predict viscosity from composition. Rather, it predicts viscosity at other wt% and temperatures from a minimal amount of experimental data.

I4.2.2 Boildown and Evaporator Data (Teats Equation)

A considerable volume of measured viscosity data has been accumulated over the years from boildown tests and evaporator runs. This discussion looks at viscosity data extracted from evaporator post run documents dating from 1982 to 1985 (Reynolds 1988). While the magnitude of the measured viscosity is not unreasonable, the observed trends are not always consistent with expectations. The following observations derived from inspection of these data:

Viscosity of solutions did not always increase with spg[1], as expected.
Viscosity measurement appears to be dependent on the instrument (the Brookfield viscometer appears to measure lower than the Haake, but this is uncertain since no sample was measured on both instruments).
Viscosity increased rapidly (particularly as measured with the Brookfield viscometer) when solutions were cooled below 30 $^{\circ}$C.

Teats selected a subset of these data (a total of 21 observations at four specific gravities) and regressed a correlation in terms of spg and temperature. The data set is provided in Table I4-5.

The Teats Equation is:

$$\ln(u) = -0.016584T - 6.208E\text{-}5T^2 + 33.58594SpG - 11.3019SpG^2 - 19.106$$

The range of applicability is for temperatures from 20 to 50 $^{\circ}$C, and for SpG from 1.0 to 1.5.

---

[1] For the purposes of this discussion, the SpG measured at 25 $^{\circ}$C identifies the sample. The SpG as well as the viscosity change with temperature.

Table I4-4. Viscosity Prediction of Aqueous Salts--NaOH.

$$U = u_o \exp[\{A + B(wt\%) + C(wt\%)^2\}/R/(T+273)]$$

	Constants		Data					Ä	Ä^2
			Wt%	Temp (°C)	Expr. Viscosity	Calc. Viscosity			
$u_o =$	1.7E-05								
A =	6346.71		0	20	1.0	0.9		0.079	0.00624
B =	57.1836		0	25	0.9	0.8		0.12167	0.0148
C =	-0.14947		0	50	0.5	0.3		0.21144	0.0148
R =	1.9872		0	75	0.4	0.2		0.21328	0.04549
			0.5	20	1.0	1.0		0.0556	0.00309
			5	20	1.3	1.5		-0.17258	0.02978
			10	30	1.4	1.6		-0.22419	0.05026
			10	70	0.7	0.4		0.27347	0.07479
			30	30	8.8	8.9		-0.09796	0.0096
			30	70	2.6	1.9		0.6837	0.46744
			50	30	40.0	40.0		0.03344	0.00112
			50	70	7.0	7.2		-0.22416	0.05025
									--------- -
									0.79757

		Predicted values		
10	40		1.1
20	50		1.8
30	45		4.8
40	45		10.0
40	30		19.3
50	60		10.7
50	35		31.5

Table I4-5. Viscosity Prediction of Aqueous Salts (from AN-105 data)

$$U = u_o \exp[\{A + B(wt\%) + C(wt\%)^2\}/R/(T+273)]$$

	Constants
$u_o =$	0.00051
$A =$	4436.47
$B =$	18.4
$C =$	0.35666
$R =$	1.9872

Data			
Wt%	Temp (°C)	Expr. Viscosity	Calc. Viscosity
0	20	1.002	1.032
0	25	0.890	0.908
0	50	0.547	0.509
0	75	0.378	0.310
0	100	0.282	0.201
37.6	28	6.000	6.225
37.6	45	4.000	3.763
37.6	65	2.500	2.221
51.3	28	20.000	19.613
51.3	45	10.000	11.150
51.3	65	7.000	6.170

Ä	Ä^2
-0.02994	0.0009
-0.0177	0.00031
0.03828	0.00147
0.0686	0.00471
0.08046	0.00647
-0.22491	0.05058
0.23724	0.05628
0.27948	0.07811
0.38655	0.14942
-1.15019	1.32294
0.82958	0.6882

	2.35939

Predicted values			
0	13		1.244
25	40		1.901
37.6	28		6.225
37.6	45		3.763
59.8	45		24.336
43.9	45		6.040
44.1	45		6.136

I4.3 CHARACTERISTICS OF ENTRAINED SOLIDS

To this date, the characteristics of entrained solids in the Phase I supernate feeds have not been determined.

I4.4 REFERENCES

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I5.0 SOLID - LIQUID SYSTEMS

Colloidal behavior is a distinct possibility with tank waste because primary particle size can be very small (<<micron). Colloidal behavior is not more widely observed because in electrolyte liquids the particles do not develop surface charges and most of the particles tend to form agglomerates and settle. Some of the terminology of colloid science is defined below:

Colloid -- a substance in a state of division too small for resolution with an ordinary light microscope, that fails to settle out of suspension and that prevents passage through a semipermeable membrane (presumably because the particles plug the membrane).

Peptize--to create a colloidal suspension, i.e., a sol.

Gelate--to form a gel from a sol.

Gel--a semisolid colloidal material formed from a sol.

Peptization has been observed at Savannah River after extensive washing reduced the ionic strength of the slurry. At Hanford, peptization has never been observed in experimental work. Hanford does not anticipate washing as extensively as Savannah River. Washed sludges will be stored in liquids of adequate ionic strength so that peptization should not be a major problem.

Nevertheless, we have to anticipate that there will be a fraction of the solids which approaches colloidal behavior. In some situations, cloudiness can persist for several weeks after agitation. A very small fraction of the solids exhibiting colloidal behavior can account for considerable turbidity.

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I6.0 WATER SOLUBILITY, CAUSTIC LEACHING AND RELATED DATA

The potential for removal by caustic leaching has been evaluated in *Status Report: Pretreatment Chemistry Evaluation FY 1997 - Wash and Leach Factors for Single-shell Tank Waste Inventory* (Colton 1997). These mass-weighted factors are suitable for modeling in composite flowsheets such as the TWRS Process Flowsheet. Wash and leach information for specific tanks and waste types can also be obtained from this reference, but they are not discussed in this section.
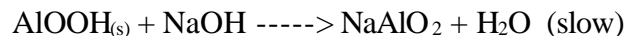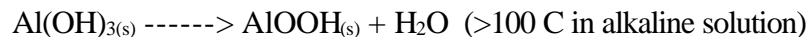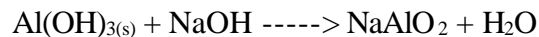
I6.1 WATER SOLUBILITY OF SINGLE-SHELL TANK WASTE

The mass-weighted average water solubility (wash factor) of SST waste is listed in Table I6-1. This wash factor represents the fraction of 18 analytes in SST waste that is water soluble upon retrieval by sluicing. The derivation of these factors does not include data for 241-C-106, which is processed during Phase I of privatization.

I6.2 CAUSTIC LEACH EFFECTIVENESS AFTER WATER WASHING

The mass-weighted average leach factor of SST waste is listed in Table 6-1. The leach factor represents the fraction of 18 analytes is SST waste that is removed by caustic leaching after water washing has previously removed water soluble species. The derivation of these factors does not include data for 241-C-106, which is processed during Phase I of privatization.

Caustic leaching appears to be capable of solubilizing gibbsite fairly rapidly. However, in some tanks the storage temperature has promoted the dehydration of gibbsite to boehmite. Conversion commences at approximately 100 C in weakly alkaline conditions. Conversion is 85 percent complete in 10.5 hrs at 150 C in 3M caustic (Weber 1982). This boehmite conversion has obviously occurred in some tanks because residual aluminum is found as boehmite as well as in some aluminosilicate species.

$$Al(OH)_{3(s)} + NaOH \text{ -----> } NaAlO_2 + H_2O$$

$$Al(OH)_{3(s)} \text{ ------> } AlOOH_{(s)} + H_2O \quad (>100 \text{ C in alkaline solution})$$

$$AlOOH_{(s)} + NaOH \text{ -----> } NaAlO_2 + H_2O \quad (slow)$$

While temperature aids in the dissolution of gibbsite, temperature may also promote dehydration to boehmite. Sludge needs to be processed at conditions that promote the dissolution of gibbsite rather than dehydration because once boehmite is formed, the redissolution is slow. Experiments have shown that boehmite can be dissolved, but extending the duration of the leach step is required.

I6.3 OXIDATIVE LEACHING DATA

The mass-weighted average oxidative leach factor of SST waste is listed in Table I6-1. The oxidative leach factor represents the fraction of 18 analytes is SST waste that is removed by oxidative leaching after water washing and caustic leaching has removed water soluble species. Oxidative

leaching is specifically targeted at converting Cr(III) to Cr(VI), although additional removal of other species is apparently achieved. Relatively few types of waste have oxidative leach data available, so the mass-weighted average factor is undoubtedly conservative.

Table I6-1. Fiscal Year 1997 Summary of Mass-Weighted Wash and Leach Factors for a Single- Shell Tank Waste.

Analyte	Wash factor[a]	Leach factor[b]	Oxidative leach factor[c]	% SST inventory accounted for
Al	24	88[d] 78[e]	7.8[d] 34[e]	101
Ba	2	0.1	Insufficient data	inventory unknown
Bi	0.2	0.3	Insufficient data	92
Ca	4	3	0.2	132
Cd	16	1	Insufficient data	76
Cr	35	78[d] 77[e]	11[d] 13[e]	80
^{137}Cs	61	78	insufficient data	115
Fe	0.3	0.7	0.1	111
Mg	2	0.3	insufficient data	inventory unknown
Mn	0.3	0.1	insufficient data	244
Na	96	46[f]	insufficient data	98
Ni	7	2	insufficient data	70
PO$_4$	79	75	5	95
Si	14	36	1	324
SO$_4$	Incomplete waste inventories--no wash and leach factors calculated.			
Sr	0.2	1	insufficient data	226
^{90}Sr	0.1	1	insufficient data	70
U	2.5	2.1	insufficient data	84
Zr	0.2	0.2	insufficient data	151

[a] Percent analyte removed from initial solids.

[b] Percent analyte removed from washed solids.

[c] Percent analyte removed from washed and leached solids using oxidative leaching methods.

[d] As a result of technical review comments, extended alkaline leach time study data, previously combined with oxidative leaching data, were combined with alkaline leach data.   This redistribution increased the leach factor and decreased the oxidative leach factor.

[e] Factors presented in June 30, 1997, draft report.

[f] Leach factor based on very limited data.

I6.4 REFERENCES

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I7.0 EFFECT OF PRIVATE CONTRACTOR UNIT OPERATIONS ON MASS BALANCES

The integrated flowsheet in the HTWOS model will account for BNFL Inc. material balance impacts in the future.

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I8.0 METHODS FOR DETERMINING GLASS COMPOSITION

Without chemical adjustment, washed sludge from pretreatment does not make glass with acceptable properties for processing and disposal. Chemical additions (typically silicon, boron and lithium) bring the stream into the processable composition envelope. There are three methods for determining the requisite amount of additives.

The first method, based on glass property models, is preferred for discrete batches of washed sludge with known composition. When sludge data does not represent an actual composition (e.g., a composite stream of all sludge), glass property modeling is not appropriate. In this case, either fixed waste loading or single component bounds is applied.

LAW waste is overwhelmingly water-soluble sodium, which drives the volume of ILAW. During immobilization, ILAW is formulated to have a nominal composition recommended in glass optimization studies.

The reader should refer to Appendix A for the details pertaining to glass loading in the HTWOS model.

I8.1 REFERENCES

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